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(54) RESIN SOLUTIONS

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis, Missouri 63166, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a pressure-sensitive resin solution and specifically to an organic solvent solution containing a chelate ester of orthotitanic acid and a resin with a functional group capable of reaction with the ester. In another aspect, the invention relates to a process for the manufacture of an article containing a film of pressure-sensitive resin.

Pressure-sensitive resins are used conventionally in the form of films to provide adhesive bonds between normally non-adhering superstrates and substrates. The films may be prepared by casting them from organic solvent solutions and evaporating the solvent.

Constraints are placed on the molecular weight of the pressure-sensitive resin by the viscosity of the solution necessary for ease of coating on commercial coating machines and by the solution concentration required for economical operation. In general, low solution viscosity and high solution concentration are desired in the pressure-sensitive resin solution, and, hence, a resin of relatively low molecular weight is preferred for film casting.

Once a bond has been made by a pressure-sensitive film placed between a substrate and a superstrate, the pressure-sensitive film may be subjected to stress generated by the weight of the superstrate or by dimensional change in the substrate or superstrate caused by thermal expansion, stress relaxation, plasticizer migration or the like. In general, a high molecular weight and a high cohesive strength is desired in the pressure-sensitive resin so that it may resist the stresses induced in the adhesive film. The opposing requirements of low molecular weight resin for ease of coating and high molecular weight resin for load holding ability are conventionally reconciled by the use of crosslinkable resin systems which can be applied at low molecular weight and cured to a high molecular weight.

Metal alkoxides are taught by Blance in U.S. Patent 3,532,708 as crosslinking agents for solution pressure-sensitive adhesives. They offer the potential of cure at room temperature merely by evaporation of the solvent. Of particular interest have been tetra-alkyl titanates which are formulated with hydroxy pressure-sensitive resins in alcohol solutions to yield stable solutions from which crosslinked pressure-sensitive resins are obtained by evaporation of the alcoholic solvent. However, such titanates particularly the lower alkyl titanates impart high solution viscosity and undesirable flow to the resin solutions.

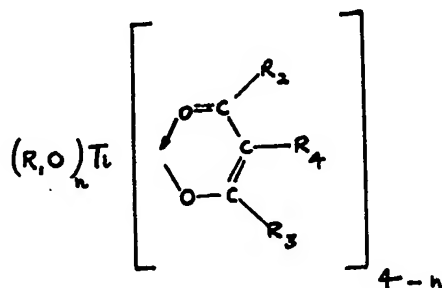
The undesirable flow is manifested by the tendency of the resin solution to form a highly extended "string" or column of fluid when a spatula or like object is pulled rapidly out of the solution. Solutions exhibiting such "stringiness" are difficult to apply on modern high-speed coating machinery. Uneven splitting and transfer of the adhesive solution on the rolls causes uneven coating. On reverse roll coaters, the formation of strings at the roll nips produces a ribbed effect in the coating and on gravure rolls, webs of solution produce coating defects.

There is, therefore, a need in the art for pressure-sensitive resin solutions with suitable viscosity and flow for application by coating rolls and which yield

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pressure-sensitive resins curable at room temperature or at slightly elevated temperatures to yield adequate cohesive strength.

The present invention provides an organic solvent solution comprising,
(i) a chelate ester having the formula



wherein n is 2 or 3, R₁ is a C₂ to C₁₀ alkyl, alkenyl, substituted alkyl or substituted alkenyl group, R₂ is a C₁ to C₆ alkyl, alkoxy, alkenyl or alkenoxy group, R₃ is a C₁ to C₆ alkyl or alkenyl group or a C₆ to C₁₀ aryl group and R₄ is hydrogen or a C₁ to C₆ alkyl or alkenyl group, and R₂ and R₃ may be combined as an ethylene or a trimethylene group; and

(ii) an interpolymers comprising:

(A) between 0.5 and 20 weight per cent of at least one monomer containing a hydroxyl, carboxyl or enolizable keto group,

(B) at least one monomer which is an ester of acrylic acid or methacrylic acid containing from 6 to 20 carbon atoms, and optionally

(C) a monomer which is an α-olefin containing from 2 to 10 carbon atoms, a C₃ to C₁₀ vinyl alkanolate, an ethyl or methyl ester of acrylic or methacrylic acid, acrylonitrile, methacrylonitrile, styrene, or vinyl chloride, wherein the interpolymers has a weight average molecular weight in the range of 10,000 to 500,000 and a glass transition temperature in the range of -15 to -75°C.;

wherein there are between 0.01 and 4 parts by weight of the chelate ester per 100 parts of interpolymers and wherein the stringiness index of the solution is less than 0.76 cm.

The invention further provides a process for preparing pressure-sensitive resin solutions with improved viscosity and flow and a process for coating them as films on substrates to provide articles of manufacture comprising films of pressure-sensitive interpolymers containing the abovedescribed chelate esters of orthotitanic acid.

The practice of the present invention involves the preparation of the interpolymers which is then formulated with the chelate ester of orthotitanic acid in a suitable organic solvent. The solution is cast on a substrate, the organic solvent is dispelled and the resulting film is cured to a creep-resistant permanently tacky composition.

The interpolymers comprises monomers selected from the groups A, B, and C described above. Group A monomers contain hydroxyl, carboxyl or enolizable keto groups. Monomers containing hydroxyl groups are exemplified by hydroxyalkyl acrylates, methacrylates, fumarates or maleates wherein the hydroxy alkyl group contains from 2 to 4 carbon atoms. Preferred hydroxy monomers include 2-hydroxyethyl acrylate or methacrylate, 2-hydroxypropyl acrylate or methacrylate, 3-hydroxypropyl acrylate or methacrylate, or bis(2-hydroxyethyl)fumarate or maleate. Monomers containing carboxyl groups are exemplified by acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, and the like, maleic acid, fumaric acid, citraconic acid, itaconic acid, and the like, and the alkyl monoesters of maleic acid, fumaric acid, citraconic acid and itaconic acid in which the alkyl group contains from 1 to 8 carbon atoms such as methyl, ethyl, propyl, butyl and octyl maleates and the like. Preferred acid monomers include acrylic acid and methacrylic acid. Monomers containing enolizable keto groups include N,N-diacetylacrylamide and N,N-diacetylmethacrylamide. The amount of group A monomer in the interpolymers is in the range of 0.5 to 20 weight per cent of the interpolymers, and is preferably in the range of 1 to 10 per cent for adequate crosslinking potential without excessive solution viscosity.

Group B monomers include the esters of acrylic and methacrylic acid

containing from 6 to 20 carbon atoms. Preferred esters contain branched chain alkyl groups such as isobutyl acrylate, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate. The pressure-sensitive resin need only contain monomers from groups A and B. However, optionally, monomers from Group C may also be present. Group C includes α -olefins containing from 2 to 10 carbon atoms, C_3 to C_{10} vinyl alkanooates such as vinyl acetate and vinyl octoate, ethyl and methyl esters of acrylic and methacrylic acids, acrylonitrile, methacrylonitrile, styrene and vinyl chloride.

The ratio of monomers in the interpolymer is selected so that the glass transition temperature is in the range of -15 to -75°C . A suitable ratio is conventionally calculated from the equation:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \dots + \frac{W_n}{T_{gn}}$$

where T_g is the glass transition temperature of the interpolymer expressed as degrees Kelvin, T_{g1} , T_{g2} , etc. are the glass transition temperatures of the homopolymers of the respective comonomers and W_1 , W_2 , etc. are the weight fractions of comonomers required for a specific glass transition temperature of the interpolymer. Glass transition temperatures are determined experimentally by conventional methods such as by means of the duPont Differential Thermal Analyzer.

The weight average molecular weight of the interpolymer is in the range of 10,000 to 500,000, corresponding to a relative viscosity in the range of 1.3 to 8.0 measured on a solution of 2 grams of interpolymer per deciliter of benzene. The preferred molecular weight range is from 20,000 to 300,000, providing adequate cohesive strength to the interpolymer without excessive solution viscosity.

The interpolymers are conveniently prepared by organic solvent polymerization techniques involving in some cases delayed addition of monomer when there is a great disparity between reactivity ratios as for example between the reactivity ratios of vinyl acetate and acrylate monomers. The time interval for the delayed addition may range from about 60 to about 600 minutes and longer. The techniques in general, involve the polymerization of the respective monomer mixtures in suitable organic solvents, the polymerization being initiated by heat activated free radical initiators.

The choice of solvents for the interpolymer used in the practice of this invention is governed by the solubility requirements of the monomers and the resulting interpolymers in that both the monomers and the resulting interpolymers should be soluble in the selected solvent or mixtures of solvents. A further preferred requirement is that the interpolymer solution should contain less than 3 per cent water by weight, based on the total weight of the solvent, in order to avoid adverse interference with the metal alkoxide component. More preferably, the interpolymer solution should contain less than 2 per cent water by weight.

Examples of suitable solvents for the interpolymers include aromatic solvents such as benzene, toluene and xylene. Suitable aliphatic solvents include esters such as ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, etc.; ketones such as methyl ethyl ketone, acetone, etc.; aliphatic hydrocarbons such as hexane and pentane. Especially useful are mixtures of the foregoing.

The polymer systems of this invention may also be prepared in mass or non-aqueous dispersion type polymerization processes as are well known to those skilled in the art. However, solution polymerization processes are preferred.

Polymerization initiators suitable for the preparation of the special interpolymers of this invention include organic peroxides, such as tert-butyl hydroperoxide, di-tert-butylperoxide, cumene hydroperoxide, di-cumyl peroxide and benzoyl peroxide. Equally suitable are organic peroxygen compounds such as tert-butyl peracetate, tert-butyl perbenzoate, di-tert-butyl perphthalate; other initiators would include α,α' -azo-di-isobutyronitrile, ultraviolet light, gamma radiation, etc.

The following preparation Examples 1 to 11 illustrate the preparation formulation and testing of the special interpolymers which are to be used in the practice of this invention and Examples A, B and C illustrate the invention. All parts and percentages are by weight unless otherwise specified and the expressions polymer and interpolymer are used interchangeably.

Preparation Example 1.

This preparation Example illustrates the preparation of an interpolymer comprising 50.5 parts 2-ethylhexyl acrylate, 45 parts methyl acrylate and 4.5 parts 2-hydroxyethyl acrylate.

The polymer is prepared under reflux conditions in a kettle equipped with a stirrer, condenser, holding tanks and pumps.

AMOUNT OF INGREDIENTS, Parts by Weight

	Initial Charge	Subsequent charges		
		1	2	3
2-ethylhexyl acrylate	14.1		6.97	
Methyl acrylate	12.6		6.20	
2-hydroxyethyl acrylate	1.26		0.62	
Ethyl acetate	19.69	12.3		9.0
Hexane	5.14		2.74	9.26
α,α' -azo-diisobutyronitrile	0.076	0.038		
Dodecyl mercaptan	0.0027	0.0013		

Charges 1 and 2 are made at uniform rates over the 1½ hour period after the initial charge reaches reflux. After 6½ hours of reflux, the batch is cooled and charge 3 is added. The solids content is 41.0 per cent. The Brookfield viscosity is 3,000 cps. The relative viscosity, determined with a solution of 2 grams of resin in 100 ml. benzene is 4.1.

Preparation Examples 2 to 11.

The general procedure of preparation Example 1 is followed except that different monomers and monomer ratios are used in order to illustrate a variety of interpolymers used in the practice of this invention.

TABLE 1.
COMPOSITIONS OF INTERPOLYMERS
PREPARED IN PREPARATION EXAMPLES 1 to 11.

Prep. Ex.	Monomeric Components	Weight Ratio
1	EHA/MA/HEA	50.5/45/4.5
2	EHA/VAc/AA	59/39.5/1.5
3	EHA/VAc/AA	52/47/1.0
4	EHA/MA/AA	61/33/6.2
5	EHA/MA/HEA	71/24/5
6	iBA/MA/HEA	71/24/5
7	VAc/EHA/HPA	45/50/5
8	VAc/EHA/HEMA	35/60/5
9	VAc/EHA/HEF	40/55/5
10	AN/EHA/HEMA	25/70/5
11	VCI/EHA/HEMA	30/65/5

LEGEND

EHA	2-ethylhexyl acrylate
MA	methyl acrylate
HEA	2-hydroxyethyl acrylate
VAc	vinyl acetate
AA	acrylic acid
HPA	3-hydroxypropyl acrylate
HEMA	2-hydroxyethyl methacrylate
HEF	bis-(2-hydroxyethyl)fumarate
AN	acrylonitrile
VCl	vinyl chloride
iBA	isobutyl acrylate

TABLE 2.

SOLUTION PROPERTIES OF INTERPOLYMERS OF PREPARATION EXAMPLES 1 to 11

SOLVENT, Weight %

Prep. Ex.	Ethyl Acetate	Toluene	Hexane	iPrOH	EtOH	Solids, %	Viscosity, cps.	Relative Viscosity
1	70	—	30	—	—	41	3,000	4.1
2	50	—	50	—	—	50	15,000	2.7
3	10	19	71	—	—	56	30,000	3.2
4	75	—	15	10	—	39	15,000	4.3
5	70	—	20	10	—	41	5,200	4.7
6	60	20	—	—	20	41	12,000	—
7	74	—	18	—	8	42	8,800	5.7
8	74	—	—	—	26	40	8,500	—
9	74	—	—	—	26	43	9,200	—
10	20	80	—	—	—	37	—	—
11	100	—	—	—	—	41	—	—

$$(R_1O)_n \left[\begin{array}{c} \text{O}=\text{C}-\text{R}_2 \\ \diagdown \quad \diagup \\ \text{O}-\text{C}=\text{C}-\text{R}_4 \\ \diagup \quad \diagdown \\ \text{O}-\text{C}-\text{R}_3 \end{array} \right]_{4-n}$$

In the evaluation of pressure-sensitive resin solutions containing esters of orthotitanic acid, the solutions are formulated to 32 weight per cent solids. The

esters of orthotitanic acid are added in ethanol solution gradually with stirring to the pressure-sensitive resin solution, the amount of ethanol being 25 weight per cent of the total solvent in the final solution.

5 The solutions are subjected to determination of viscosity and "stringiness index". Viscosity is determined at 20°C. by the conventional method using a Brookfield Model LVF Viscometer and the appropriate spindle and speed. Viscosity stability is determined from viscosity measurements over a 7 day period. 5

10 The stringiness index (S.I.) is determined by immersing a platinum surface tension ring of 3.6 cm diameter, one inch below the surface of the pressure-sensitive resin solution contained in a 7.62 cm diameter jar. The ring is mounted in the jaw of an Instron Test Machine and is withdrawn from the solution by allowing the crosshead upon which the jar rests to descend at a rate of 12.7 cm/min. ("INSTRON" is a registered Trade Mark). The tensile force exerted on the ring is recorded by means of the A cell on the chart set at 10 grams full scale and moving at 12.7 cm/min. The stringiness index is measured from the peak of maximum extensional force to the failure point of the elongating curtain of solution. Five measurements are made in rapid succession. The arithmetic average expressed in centimetres is the stringiness index. In general, a stringiness index of less than 0.76 cm indicates that a resin solution has good flow properties and that the solution will not form strings on conventional high-speed roll coaters at normal speeds of operation. The tendency of a pressure-sensitive resin solution to develop stringiness is determined by measurement of the stringiness index over a 7 day period. 10 15 20

EXAMPLE A.

25 The data for viscosity and stringiness index of the interpolymer solutions of preparation Examples 1—4 formulated with various esters of orthotitanic acid are presented in Tables 3 and 4. The solids content of the solutions is 32 per cent. Ethanol forms 25 per cent of the solvent. In the Tables, TBT signifies tetrabutyl titanate and TAA signifies di-isopropoxy titanium diacetylacetonate which is formed by reaction of 2 moles of acetylacetone with 1 mole of tetra-isopropyl titanate. 25 30

TABLE 3.

EFFECT OF TITANATE TYPE ON SOLUTION VISCOSITIES (viscosities in cps.)
RESIN

Titanate		Prep. Example 1		Prep. Example 2		Prep. Example 3		Prep. Example 4	
Concentration, grams per 100 g. resin	Type	Initial	Aged 1 week	Initial	Aged 1 week	Initial	Aged 1 week	Initial	Aged 1 week
0	none	800	850	195	180	375	380	—	—
0.2	TBT TAA	1,170 810	1,140 840	270 235	280 240	535 415	560 410	—	—
0.4	TBT TAA	1,920 870	1,800 900	470 300	500 345	1,110 450	1,200 460	Gel 7,700	Gel 14,000
0.6	TBT TAA	Gel 940	Gel 1,000	1,130 250	1,350 250	2,550* 455	3,000* 480	Gel 9,000	Gel 18,000

* Very ropy, stringy; not coatable.

TABLE 4.

EFFECT OF TITANATE TYPE ON "STRINGINESS INDEX" (in inches)

RESIN

Titanate		Prep. Example 1		Prep. Example 2		Prep. Example 3	
Concentration, grams per 100 g. resin	Type	Initial	Aged 1 week	Initial	Aged 1 week	Initial	Aged 1 week
0	None	0.18	0.21	0.23	0.19	0.13	0.14
0.2	TBT TAA	0.22 0.18	0.25 0.21	0.21 0.20	0.30 0.29	0.14 0.18	0.17 0.18
0.4	TBT TAA	0.35 0.20	0.27 0.19	0.37 0.18	0.41 0.26	0.21 0.18	0.20 0.18
0.6	TBT TAA	— 0.20	— 0.22	0.39 0.22	0.53 0.27	0.64 0.18	0.72 0.18

The data show the higher viscosities, the tendency to gel and the higher stringiness indices of pressure-sensitive resin solutions containing tetrabutyl titanate in comparison with solutions containing diisopropoxy titanium diacetylacetonate especially at higher concentrations of the titanate ester.

Data for stringiness index of interpolymer solutions of preparation Examples 3 and 6 through 11 formulated with various chelate esters of orthotitanic acid are presented in Table 5. The solids content of the solutions is 30 per cent. Ethanol forms 25 per cent of the solvent. The concentration of chelate ester of titanium is 0.4 parts per 100 parts by weight of resin.

EXAMPLE B.

The pressure-sensitive resin solutions listed in Table 3 are cast on silicone release paper, and the cast films are dried at room temperature then at 90°C. for 2 minutes to dispel the organic solvent. The (0.002 cm thickness) films are cooled to room temperature and applied to polyvinyl chloride film (Ultron Polyvinyl Chloride UL—58 Film, 0.0076 cm thick, supplied by Monsanto Company). The laminate is cut into 2.54 cm strips. The strips are conditioned at 22°C and 50% relative humidity for 24 hours. The release paper is removed and the strips are applied to steel panels (ASTM 1000—65) with a Pressure-Sensitive Tape Council roller. Peel strength is determined on an Instron Test Machine by peeling the strip at a 180° angle and at a rate of 15.1 cm per minute from the steel panel. "Green" strength is gauged by comparing the peel strength of the bond 20 minutes after formation and 24 hours after formation. Data are presented in Table 6.

TABLE 5.

STRINGINESS INDEX OF INTERPOLYMER SOLUTIONS CONTAINING CHELATE ESTERS OF ORTHOTITANIC ACID

Resin Prep. Ex.	TITANIUM CHELATE ESTER			Stringiness Index (cm)
	n	R ₁	Chelating Agent	
3	2	iso-propyl	acetylacetone	<0.76 cm
6	3	iso-propyl	acetylacetone	<0.76 cm
7	2	octyl	benzoylacetone	<0.76 cm
8	2	butyl	1,3-cyclohexanedione	<0.76 cm
9	2	octyl	1,3-cyclopentanedione	<0.76 cm
10	2	butyl	ethyl acetoacetate	<0.76 cm
11	2	iso-propyl	acetylacetone	<0.76 cm

TABLE 6.

PEEL STRENGTH OF PRESSURE-SENSITIVE RESINS (gm/cm width)

Titanate		RESIN					
Concentration, grams per 100 g. resin	Type	Prep. Example 1		Prep. Example 2		Prep. Example 3	
		20 min.	24 hr.	20 min.	24 hr.	20 min.	24 hr.
0	none	678.7	714.4	893.0	1536.0 [*]	750.1	839.4
0.2	TBT TAA	589.4 607.2	714.0 678.7	714.0 660.8	1250.2 [*] 1339.5 [*]	696.5 643.0	785.8 821.6
0.4	TBT TAA	535.8 535.8	696.5 750.1	553.7 535.8	857.3 982.3	660.8 571.5	750.1 750.1
0.6	TBT TAA	— 535.8	— 625.1	446.5 482.2	785.8 863.7	— 517.9	— 714.0

* Subscript "c" denotes cohesive splitting of the film.

The data show that titanate ester causes a decrease in peel strength in direct relation to the concentration of titanate ester. However, the effects of tetrabutyl titanate and diisopropoxy titanium diacetylacetonate are essentially equivalent and in no case is the peel strength reduced below a useful value.

The cohesive strength of the pressure-sensitive adhesive is gauged from the creep resistance of a 1.61 cm² 0.002 cm thick bond formed by the film of adhesive between a strip of Mylar Polyester film (a product of E. I. duPont de Nemours and Company) and a polished stainless steel bar ("MYLAR" is a registered Trade Mark). The Mylar strip is loaded with a one-pound weight. The bond is held in a vertical plane at 22°C and 50% relative humidity and the time in hours for failure after application of the load is determined. The data are presented in Table 7.

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TABLE 7.
CREEP RESISTANCE OF PRESSURE-SENSITIVE RESINS
(hours to failure)

Titanate		RESIN			
Concentration, g. per 100 g. resin	Type	Pr. Ex. 1	Pr. Ex. 2	Pr. Ex. 3	Pr. Ex. 4
0	none	0.2	0.3	0.7	0.5
0.2	TBT	3	3	4.6	—
	TAA	3	2	4	10
0.4	TBT	10	55	40	—
	TAA	25	15	55	25
0.6	TBT	—	52	—	—
	TAA	55	145	155	—

Note that at low concentrations of titanate ester, the initial creep resistance is roughly the same for resins containing tetrabutyl titanate and those containing diisopropoxy titanium diacetylacetonate; but at higher concentrations, the creep resistance improves to a higher level for TAA formulations than for the TBT systems. An exception is the preparation Example 2 system for which TBT may be a more efficient crosslinker.

This invention also contemplates the use of fillers, extenders, stabilizers, antioxidants, plasticizers, tackifiers, flow control agents, adhesion promoters, dyes, etc. in the pressure-sensitive resin solutions and the pressure-sensitive resins of this invention.

The compositions of the present invention may be used as the adhesive component in pressure-sensitive tapes, films and foams. They adhere well to resin surfaces such as plasticized polyvinyl chloride, polyethylene terephthalate such as Mylar, cellulose acetate, nylon, polyethylene, polypropylene, paper, or silicone-coated paper as well as metal and painted surfaces. They are especially useful as the adhesive component of decorative vinyl sheets and decals, conferring excellent shrink resistance to vinyl film. Their excellent tack retention, creep resistance and resistance to plasticizer migration make them useful as adhesives for vinyl foam and tiles. Their outstanding tack, wetting and holding power may be used to advantage in transfer adhesive applications.

Articles of manufacture such as tapes, decals, decorative vinyl sheets and transfer films containing the pressure-sensitive resin composition of the present invention are prepared by coating the resin on the appropriate substrate by conventional coating methods. Such articles conventionally include a release paper for temporary protection of the adhesive film until the adhesive bond is made. The thickness of the adhesive film is generally in the range of 0.00051 to 0.0127 cm.

Application of the film to the substrate is conventionally carried out on roll coaters such as reverse roll and gravure roll coaters. The resin solution viscosity is adjusted to between 25 and 5,000 centipoises with higher viscosities within the range preferred for reverse roll coating and lower viscosities within the range preferred for gravure coating. The coatings are applied to the substrate moving through the rolls at a rate of between 5.1 cm/sec. and 508.0 cm/sec.

Example C.

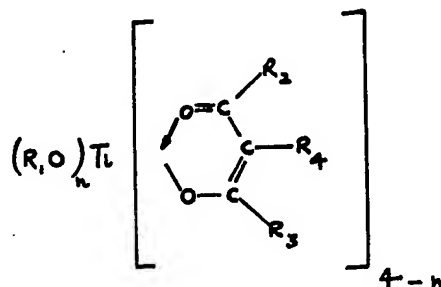
This Example is set forth to compare the performance of a resin solution formulated with tetrabutyl titanate with a resin solution formulated with diisopropoxy titanium diacetylacetonate in reverse roll application to a poly(vinyl chloride) substrate at a rate of 25.4 cm/sec.

Polymer solutions made according to preparation Example 1 are diluted to 30 per cent solids and formulated with 0.5 parts tetrabutyl titanate or diisopropoxy titanium diacetylacetonate per 100 parts of resin. The levels of titanate compound are selected to give the desired cohesive strength in the dried films. The TBT solution had a Stringiness Index of about 0.45 and gives poor coatings of rough

surface texture and uneven thickness. A large number of "strings" are observed between the application roll and the substrate during the coating operation. These coatings are judged unsuitable for commercial use. The TAA solution has a Stringiness Index of about 0.20 and gives smooth coatings of uniform thickness. These films are judged satisfactory for commercial use.

WHAT WE CLAIM IS:—

1. An organic solvent solution comprising:
 - (i) a chelate ester having the formula



wherein n is 2 or 3, R₁ is a C₂ to C₁₀ alkyl, alkenyl, substituted alkyl or substituted alkenyl group, R₂ is a C₁ to C₆ alkyl, alkoxy, alkenyl or alkenoxy group, R₃ is a C₁ to C₆ alkyl or alkenyl group or a C₆ to C₁₀ aryl group and R₄ is hydrogen or a C₁ to C₆ alkyl or alkenyl group, and R₂ and R₃ may be combined as an ethylene or a trimethylene group; and

- (ii) an interpolmer comprising:

(A) between 0.5 and 20 weight per cent of at least one monomer containing a hydroxyl, carboxyl or enolizable keto group,

(B) at least one monomer which is an ester of acrylic acid or methacrylic acid containing from 6 to 20 carbon atoms, and optionally

(C) a monomer which is an α-olefin containing from 2 to 10 carbon atoms, a C₃ to C₁₀ vinyl alkanoate, an ethyl or methyl ester of acrylic or methacrylic acid, acrylonitrile, methacrylonitrile, styrene, or vinyl chloride, wherein the interpolmer has a weight average molecular weight in the range of 10,000 to 500,000 and a glass transition temperature in the range of -15 to -75°C.;

wherein there are between 0.01 and 4 parts by weight of the chelate ester per 100 parts of interpolmer and wherein the stringiness index of the solution is less than 0.76 cm.

2. A resin solution according to Claim 1 in which the chelate ester is the reaction product of a tetraalkyl or tetraalkenyl titanate wherein the alkyl or alkenyl group contains 2 to 10 carbon atoms, and an enolizable keto compound which is acetylacetone, benzoylacetone, 1,3-cyclopentandione, 1,3-cyclohexandione, or an alkyl acetoacetate or a C₁ to C₆ alkyl or alkenyl substituted derivative thereof, the mole ratio of tetraalkyl or tetraalkenyl titanate to enolizable keto compound being in the range of 1:1 to 1:2.

3. A resin solution according to Claim 2 in which the enolizable keto compound is acetylacetone.

4. A resin solution according to any of Claims 1 to 3 in which the interpolmer comprises a hydroxy monomer which is 2-hydroxyethyl acrylate or methacrylate, 2-hydroxypropyl acrylate or methacrylate, 3-hydroxypropyl acrylate or methacrylate, bis(2-hydroxyethyl) fumarate, or bis(2-hydroxyethyl) maleate.

5. A resin solution according to Claim 4 characterized wherein said interpolmer comprises 2-ethylhexyl acrylate and 2-hydroxyethyl acrylate.

6. A resin solution according to any of Claims 1 to 3 in which the interpolmer comprises a carboxy monomer which is acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid, citraconic acid, itaconic acid or an alkyl mono ester of maleic acid, fumaric acid, citraconic acid, or itaconic acid in which the alkyl group contains from 1 to 8 carbon atoms.

7. A resin solution according to any of Claims 1 to 3 in which the interpolmer comprises 2-ethylhexyl acrylate and acrylic acid, methacrylic acid, N,N-diacytonyl-acrylamide or N,N-diacytonylmethacrylamide.

8. A resin solution according to any of Claims 1 to 7 containing less than 3 weight per cent of water based on the total weight of the solvent.
9. A resin solution according to any of Claims 1 to 8 in which the solids content is from 10 to 60% by weight.
- 5 10. A resin solution according to Claim 1 in which the interpolymers are substantially as described in any one of Preparation Examples 1 to 11. 5
11. A resin solution according to Claim 1 substantially as described in the non-comparative portion of Example A.
- 10 12. A process for the production of film of pressure sensitive adhesive which comprises coating a substrate with a resin solution according to Claim 1, dispelling the solvent therefrom and curing the resulting film. 10
13. A process according to Claim 12 in which the substrate is a film of plasticized polyvinyl chloride, polyethylene terephthalate, cellulose acetate, nylon, polyethylene, polypropylene, paper or a silicone-coated paper.
- 15 14. A process according to either of Claims 12 and 13 in which the resin solution has the features of any one of Claims 2 to 11. 15
15. An article coated with a film of pressure-sensitive adhesive resin prepared by a process according to any of Claims 12 to 14.
- 20 16. A process for the production of an article according to Claim 15 substantially as described in Example B. 20

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